



XPS and UPS investigation of the diamond surface oxidation by UV irradiation

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ABSTRACT

In this work we describe the effect of oxidation on undoped nanocrystalline H-terminated CVD diamond films. Surface oxidation was performed using UV photons in air and in pure dry oxygen atmosphere. The samples were then thermally treated to study the effect of the UV-induced oxidation on the electronic properties of diamond. Different annealing temperatures were applied to induce a controlled oxygen desorption. Both UV- and X-ray photoelectron spectroscopies were performed *in situ* in order to correlate the electron affinity changes to the oxygen atomic abundances detected on the diamond surfaces. Our results show that UV oxidation is less invasive if compared to other conventional processes like chemical or plasma oxidations. This enables a recovering of the surface electronic properties with the thermal desorption of oxygen from the diamond surfaces.

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1. Introduction

Diamond, thanks to its outstanding electrochemical properties, is a very promising material for realizing electronic and biochemical devices [1–3]. In fact, the electrochemical surface properties of diamond may be changed by appropriate functionalizations. The hydrogen termination leads to conductive diamond surfaces while the oxidation renders them non-conductive [4]. Considering additional degree of complexity, the diamond terminated surfaces may be grafted with ammine groups which behave as active sites to bond specific biomolecules allowing surface bioengineering [5,6]. Concerning diamond oxidation, irradiation with UV-photons was recently proposed [7]. This oxidation technique is very promising allowing functionalization of selective regions of the diamond surface in order to realize sensors [8]. Although the use of UV irradiation is widely used, the chemical processes related to the ozone interaction with the H-terminated diamond surface remain still not completely clarified. It is well known that different surface terminations of the diamond surface lead to a strong modification of the electronic structure of diamond. In particular, a fully H-terminated surface shows a negative electron affinity (NEA) while an oxidized diamond surface exhibits a positive electron affinity (PEA) and insulating properties. Direct determination of NEA–PEA parameters is generally performed using

Kelvin probes while, as in our case, indirect estimation of the diamond electron affinity is obtained via UV photoelectron spectroscopy (UPS). In HeI-UPS the secondary electron peak appears as a sharp feature whose position (the cut off) determines the minimum detectable kinetic energy (i.e. the maximum of binding energy referred to E_F) of electrons leaving the diamond surface into the vacuum. The HeII photons allow the estimation of the valence band maximum (VB_M) respect to E_F . Observe that here we use of E_F as a reference for the HeI, HeII spectra, i.e. a binding energy scale. Differently from the vacuum level (the reference for kinetic energies) which changes with the surface work function, E_F is fixed and this makes of all the calculation easier. Combining cut-off and VB_M , the electron affinity χ of the diamond sample can be calculated as:

$$\chi = h\nu - E_g - W \quad (1)$$

where $h\nu$ is the photon energy, E_g is the diamond band gap (5.5 eV), and W is the emission width [9] namely the difference between the VB_M and the cut-off positions. These positions are obtained with linear extrapolations of the HeI, HeII spectra as described in [10,11]. Applying the simple relation (Eq. (1)) in a previous work we showed that the diamond exposure to UV light in atmosphere is able to induce a surface oxidation and the correspondent changes of the electron affinity from NEA to PEA [12]. In this work we present a detailed study of the electron affinity modifications induced by thermal treatments applied to the oxidized diamond surface. It is known that high temperature annealing is able to induce oxygen desorption from the

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Table 1

The thermal treatments (TT) performed on the two diamond samples HNCDA and HNCDB.

	HNCDA			HNCDB		
	T (°C)	Time (min)	χ (eV)	T (°C)	Time (min)	χ (eV)
Cleaning	400	30	-1.26	400	30	-1.55
Oxidation	//	180 ^a	1.70	//	240 ^b	0.70
TT1	400	30	0.89	300	30	0.15
TT2	400	30	0.64	400	30	0.08
TT3	600	30	0.31	600	30	-0.04
TT4	700	30	0.30	800	30	-0.17
TT5				970	30	-0.28

^a Performed in air.

^b Performed *in situ*.

diamond surface. Here we will show that oxygen desorption starts at rather low temperatures and at higher temperatures it leads to a recovery of a negative electron affinity.

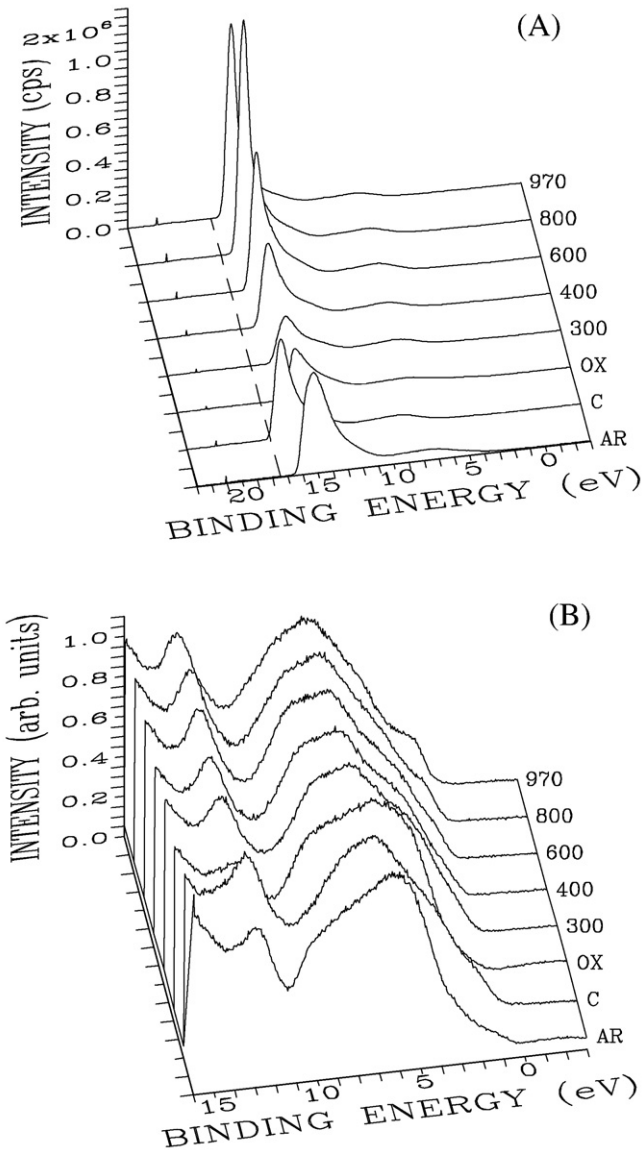


Fig. 1. (A) Hel (21.2 eV) spectra of HNCDB diamond as a function of the treatments applied. The dashed line is placed in correspondence of the cleaned H-terminated diamond cut-off. (B) The correspondent HeII (40.8 eV) spectra of the virgin and treated diamond surfaces. AR, C and OX means 'as received', 'cleaned' and 'oxidized' respectively, numbers refer to annealing temperature (°C).

2. Experimental

Nano-crystalline diamond films (NCD) produced by hot filament CVD process were hydrogen terminated (HNCD) using a microwave-assisted hydrogen plasma at 600 °C. The samples were cooled down to room temperature under H₂ flux for about 90 min (see also [12] for more details).

The samples were transferred in an ultra high vacuum analysis chamber provided with a double pass cylindrical mirror analyzer (PHI550), an UV- and an X-ray source with photon energies of 21.2 eV, 40.8 eV and 1253.6 eV respectively. The cleaning procedure applied to the two NCD, consisted of a thermal treatment at 400 °C for 30 min performed *in situ*. This ensures the removal of the surface contaminants preserving the full hydrogenation of the surface. The samples were then characterized by XPS to quantify the abundance of residual oxygen present on the surface due to the non-diamond grain boundaries.

In the case of HeI spectra, the samples were biased applying a 4 V voltage to compensate the analyzer work function and to ensure that low-energy electrons of the secondary peak are correctly measured. The Au Fermi Edge was acquired prior to any spectral acquisition to calibrate the binding energy scale. The two diamond surfaces were then oxidized at room temperature using two different processes: (i) irradiation with Xe-UV source at 400 W (lamp 1) performed in air for 3 h and (ii) irradiation with Deuterium-UV source at 25 W (lamp2) performed *in situ* in pure dry oxygen for 4 h. A series of thermal treatments were then applied *in situ* to the oxidized diamond surfaces (see Table 1) up to 970 °C. The electron affinity and the oxygen abundance were measured after oxidation and each of the thermal treatments.

3. Results

The effect of the surface treatments is shown in Fig. 1. The sequence of HeI spectra in Fig. 1A clearly shows the change in the cut-off position (the dashed line is added as a guide for the eye). In particular the cut-off of the second spectrum which corresponds to the cleaned hydrogenated diamond is placed at 17.7 eV the high value on the binding energy scale (BE) among the HeI spectra. Oxidation induces a strong decrease of the secondary electron peak. Although qualitative, variations of spectral intensity of the secondary electrons are linked to the electron affinity of the diamond surfaces [13]. Interestingly, the intensity of the secondary electron peak increases step by step with the application of the thermal treatments. In Fig. 1B the correspondent HeII spectra are shown. Again the cleaning process leads to a strong

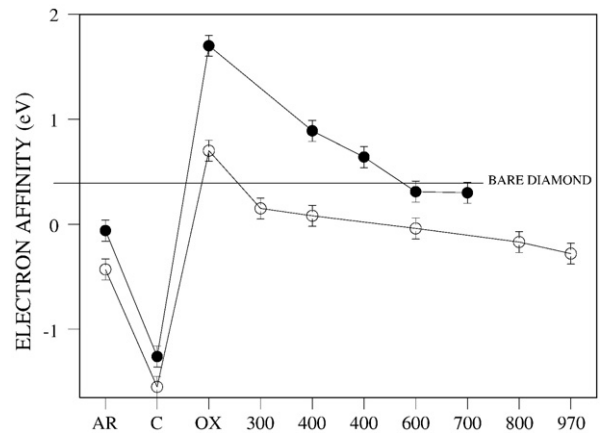


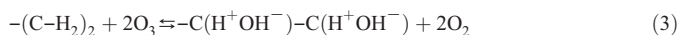
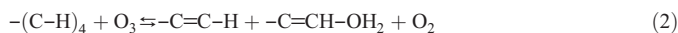
Fig. 2. Trend of the electron affinity on the sample HNCDA (black circles) and HNCDB (white circles) as a function of the surface treatments carried out along the experiment. On the abscissa AR, C and OX means 'as received', 'cleaned' and 'oxidized' respectively, numbers refer to annealing temperature (°C).

change in the diamond density of states (DOS) leading to a valence band (VB) in agreement with literature. Both the oxidation processes induce an evident strong modification of the VB. As it can be seen in the third HeII spectrum, there is a prominent band broadening due to the appearance of the oxygen 2s component at ~5 eV. Also the feature at ~13 eV flattens and moves to higher BE. As for the HeI spectra, also in this case the application of the thermal annealing leads to a progressive decrease of the oxygen-related features. As a consequence the VB becomes similar to the original H-terminated diamond spectrum. The HeI, HeII spectral changes induced by oxidation and thermal treatments on the diamond electronic properties are mirrored by the behavior of the electron affinity χ . Fig. 2 displays the trend of χ as a function of the applied surface treatment. The first annealing at 400 °C induces a reduction of the χ due to the desorption of the contaminants. Oxidation causes an abrupt increase of χ with a transition from NEA to PEA. The successive thermal treatments lead to a progressive decrease of the electron affinity which for the highest values of temperature becomes negative again. To appreciate the effect of the *in situ* UV irradiation, Fig. 3A shows the survey of cleaned and oxidized diamond surface. Finally Fig. 3B represents the trend of the oxygen concentration O% in the two samples. O% was estimated from the XPS spectra acquired after oxidation and each annealing treatment. As for the electron affinity, the minimum values correspond to the cleaned H-terminated sample while the maximum value is found in correspondence of the oxidation treatment. Then a regular

decrease is observed along with the increasing of the temperature of the annealing treatments, as expected.

4. Discussion

Two different oxidation processes are investigated in this work. In the case of sample HNCDA the sample was irradiated in air while in the case of sample HNCDB the oxidation was performed *in situ* in a pure dry oxygen atmosphere. This allowed us to determine whether the influence of the ionic species present in the atmosphere is or is not able to trigger changes in the diamond DOS. The two kinds of UV irradiations showed different efficiencies in oxidizing the diamond surfaces. In the case of sample HNCDA after the UV-oxidation, the oxygen abundance estimated from XPS was 5.6%. Although the power of the lamp2 was much lower than that of lamp1, the efficiency of the *in situ* oxidation was higher since a 8.2% of oxygen concentration was found on the HNCDB sample. Apart from the quantities of oxygen found on the two diamond surfaces, the results of the experiment in the two cases are comparable. As it appears from Fig. 2, the trend of χ is the same in the two HNCDA samples. The different trends of the electron affinity may be explained considering the different influence of the UV activated air components and ozone on the electrical properties of the diamond surfaces. Plasma and chemical processes used to oxidize diamond produce strong covalent C–O bonds with a strong electron localization and surface dipoles re-orientation towards the diamond bulk [14]. The combination of these two effects causes a NEA to PEA transition. For an oxidized diamond surface the PEA ranges between 1.0 eV and 1.7 eV [15] and lowers to ~0.5 eV in the case of polycrystalline diamond [16]. This variability may depend on different extent of surface oxidations [15] and on the non-diamond grain boundaries. Table 1 summarizes the values of χ of our diamond samples as a function of the surface treatments. Fig. 2 shows that after UV oxidation in air, the electron affinity of the sample HNCDA increases up to 1.7 eV in agreement with previous data [4]. The application of the thermal treatments to our UV-oxidized samples lead to unexpected results. Oxygen desorption from an oxidized diamond is known to progressively decrease the value of χ since C–O bond breaking leads to π bonds [17,18] characterized by a PEA of 0.4 eV [4]. The results of our experiments indicate a different surface evolution. The successive application of thermal treatments with loss of oxygen from the diamond surface leads to a recovery of the original χ values. For both the diamond films the electron affinity becomes negative even if the different annealing temperatures and the different oxygen concentrations brought to different electron affinities. The recovery of the H-terminated surface may be explained on the basis of specific chemical reaction occurring at the diamond surface induced by the UV irradiation. This oxidation process is based on the ability of UV photons to create O radicals. On the basis of chemical grounds and theoretical modeling, the authors hypothesized the presence of weak interactions between those radicals and the diamond surface:



This explains also the results shown in Fig. 3 where the amount of oxygen significantly decreases at only 300 °C since much less energy is required to break interactions respect to strong covalent C–C bonds leading to desorption of CO, CO₂. When the weak ionic bonds break, oxygen leaves the diamond surface and hydrogen is replaced in its initial site thus reducing the surface electron affinity. These results point to the conclusion that the UV-induced oxidation implies different kinds of chemical reactions respect to oxidations performed via plasma or wet chemical reaction. Thanks to the formation of non-

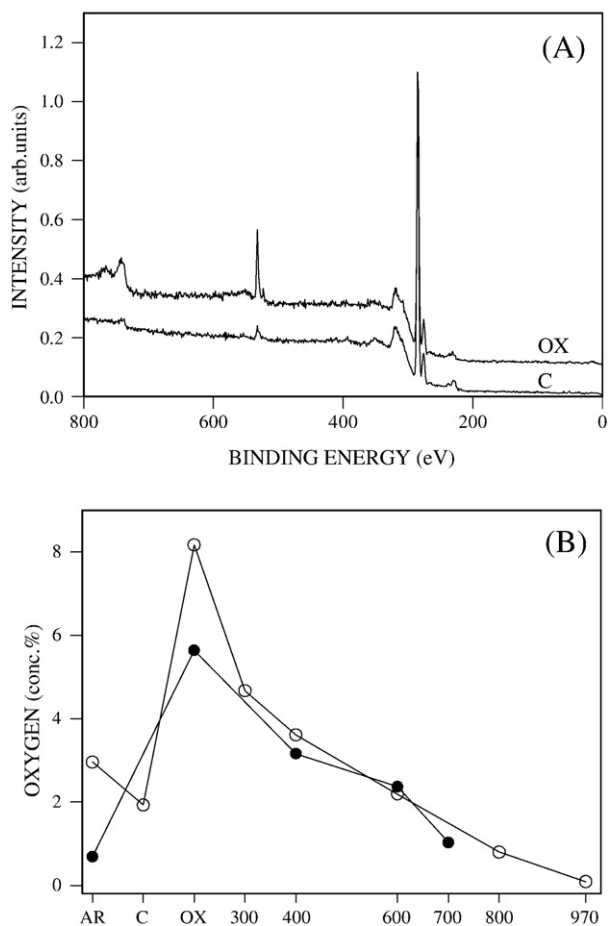


Fig. 3. (A) Survey spectra from hydrogenated diamond surface after the cleaning process (C) and after the *in situ* UV-oxidation (OX) diamond. (B) Oxygen atomic abundance as estimated from XPS spectra in relation to the surface treatments performed. Black circles refer to sample HNCDA, white circles refer to HNCDB. On the abscissa AR, C and OX means 'as received', 'cleaned' and 'oxidized' respectively, numbers refer to annealing temperature (°C).

covalent weak interactions the UV-induced oxidation is partially reversible.

5. Conclusion

In this work the effect of annealing on UV oxidized NCD samples was studied. At this aim two different kinds of oxidation were considered: UV irradiation in air and UV irradiation *in situ* in pure O₂ atmosphere. Apart from the different oxidation efficiencies the two processes of diamond oxidation led to similar results. The diamond electron affinity and the extent of oxidation were evaluated by UPS and XPS analysis respectively. By decreasing the oxygen concentration on the diamond surface a decrease of the electron affinity was observed. The sequence of thermal treatments applied to the diamond samples led to negative values of the electron affinity. The considerable reduction of the oxygen concentration at low temperature and the recovery of the NEA, have been explained on the basis of specific weak interactions induced by the UV irradiation.

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